

A-site substitution effect on physical properties of $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$

J. Tozawa, M. Akaki, D. Akahoshi, H. Kuwahara, and K. Itatani

Faculty of Science and Technology, Sophia University, Tokyo 102-8554, Japan

E-mail: j-tozawa@sophia.ac.jp

Abstract. We have investigated the Ln^{3+} -substitution (Ln = lanthanoid) effect of a quasi two-dimensional ferromagnet $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ ($x=0.5$). With increasing Ln^{3+} -concentration, the ferromagnetism is gradually suppressed and the resistivity is increasing, which are ascribed to an increase in antiferromagnetic (AFM) clusters created by Ln^{3+} -substitution. In $\text{Sr}_{2.7}\text{Gd}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$, the magnetoresistance (MR) is enhanced by about 20 % compared with that of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$. Coexistence of ferromagnetic (FM) and AFM phases is essential for the enhancement of the MR. Applied magnetic fields align the FM clusters in the same direction, resulting in a reduction in the resistivity. A metamagnetic transition observed in the Ln^{3+} -doped samples also contributes to the enhancement of the MR.

1. Introduction

Since the discovery of the colossal magnetoresistance (CMR) effect, Mn oxides with a perovskite structure and their derivatives have been intensively investigated. In particular, two-dimensional ferromagnetic (FM) metal $(\text{La}, \text{Sr})_3\text{Mn}_2\text{O}_7$ has been attracting much attention because such metals are rarely reported. $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ can be expected as one of such rare materials[1, 2]. The end material $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ is an antiferromagnet below $T_N = 120$ K, and changes from a semiconductor to a metal at 350 K[3]. With increasing Co-concentration, this system approaches an FM metal and negative magnetoresistance (MR) is observed. Ghosh *et al.* suggest that the ferromagnetism is driven by spin-dependent electron transfer processes between Fe^{4+} and Co^{4+} [4]. Since highly oxidized states of both Fe^{4+} and Co^{4+} are unstable, the crystal structure of $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ has a large amount of oxygen vacancies. The oxygen deficiency δ of $\text{Sr}_3\text{Fe}_{1.4}\text{Co}_{0.6}\text{O}_{7-\delta}$ treated under high oxygen pressure of 600 bar at 1173 K is 0.20 ± 0.01 [4]. A decrease in the average valence of B -site cations weakens the spin-dependent electron transfer process, which probably leads to coexistence of FM and AFM (or PM) phases. Such phase coexistence can be expected to enhance the MR of $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$, as is often the case with CMR manganites. In this study, in order to enhance the MR, we have prepared Ln -substituted $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ and have investigated the physical properties.

2. Experiment

$\text{Sr}_{3-y}\text{Ln}_y\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ was prepared in a polycrystalline form by a solid-state reaction method. Mixed powders of SrCO_3 , Ln_2O_3 ($Ln = \text{La}, \text{Nd}, \text{and Gd}$), Fe_3O_4 , and CoO were heated at 1173 K in air and sintered at 1673 K in O_2 . The sample was then annealed under high oxygen pressure of 240 bar at 773 K for 10 h, and cooled down to about 300 K at a rate of 40 K/h.

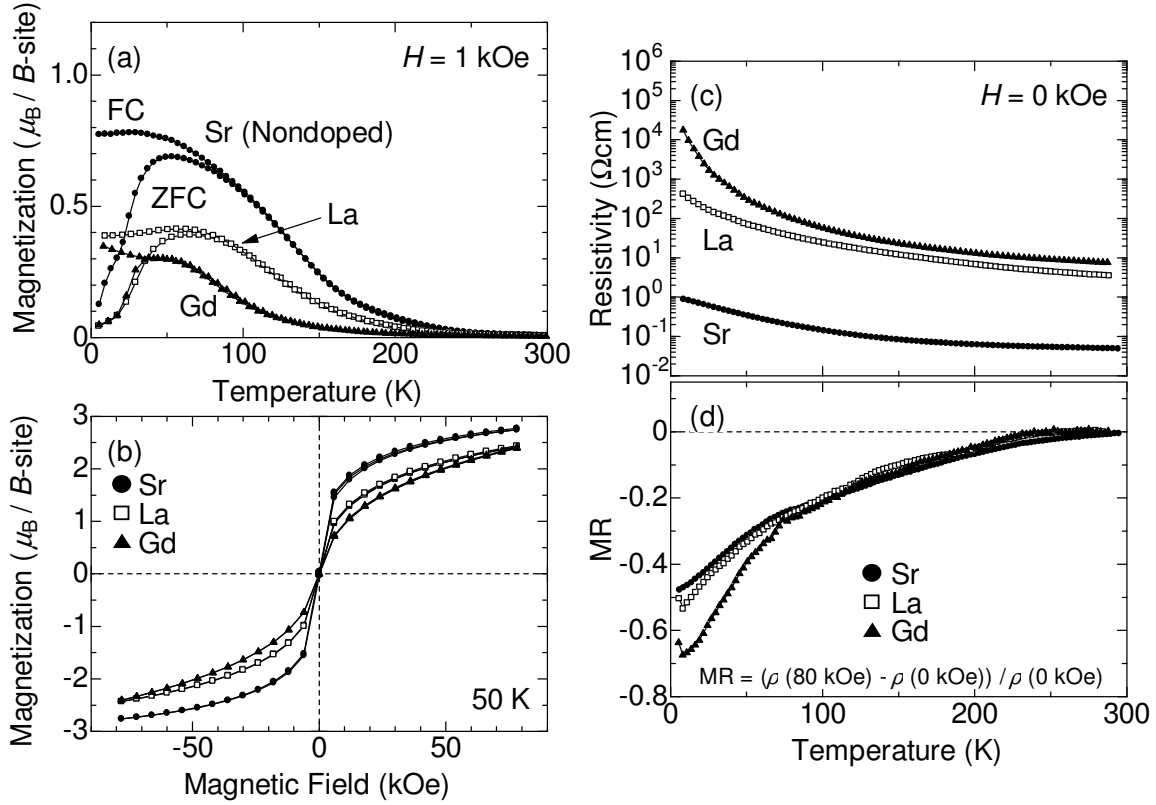
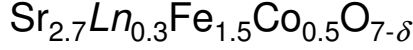


Figure 1. (a) Temperature and (b) magnetic field dependence of magnetization of $\text{Sr}_{2.7}\text{Ln}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ ($\text{Ln} = \text{La}$ and Gd). A nondoped sample is also presented for comparison. Temperature dependence of (c) resistivity in a zero field and (d) magnetoresistance (MR). Here the MR is defined as $\text{MR} = (\rho(80 \text{ kOe}) - \rho(0 \text{ kOe})) / \rho(0 \text{ kOe})$.

Crystallographic analysis of the obtained samples was performed by X-ray diffraction method at room temperature. The oxygen content of the synthesized samples was estimated using iodometric titration with an accuracy of ± 0.02 . The magnetic properties were measured using a Quantum Design, Physical Property Measurement System (PPMS - 9T). The resistivity was measured using a standard four-probe method.

3. Results and discussion

Figures 1 (a) and (b) show the temperature dependence of the magnetization (M - T) and magnetization curves (M - H) of $\text{Sr}_{2.7}\text{Ln}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ ($\text{Ln} = \text{La}$ and Gd). The M - T of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ shows an increase below 250 K. The zero field cooling (ZFC) process deviates from field cooling (FC) below 80 K. The magnetization is FM below 250 K, and the magnetization value reaches about $2.8 \mu_B / \text{B-site}$ at 50 K, as seen from the M - H curve. These magnetic behaviors result from the emergence of the cluster glass state, as previously reported[1]. This cluster glass-like behavior is prominent below 80 K. In $\text{Sr}_{2.7}\text{La}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$, the onset temperature of the FM transition shifts to lower temperatures, and the FM moment is slightly suppressed (Fig. 1(b)). In the case of Gd^{3+} -substitution, the FM moment is close to that of $\text{Sr}_{2.7}\text{La}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$, but the FM transition temperature is further lower to around 150 K.

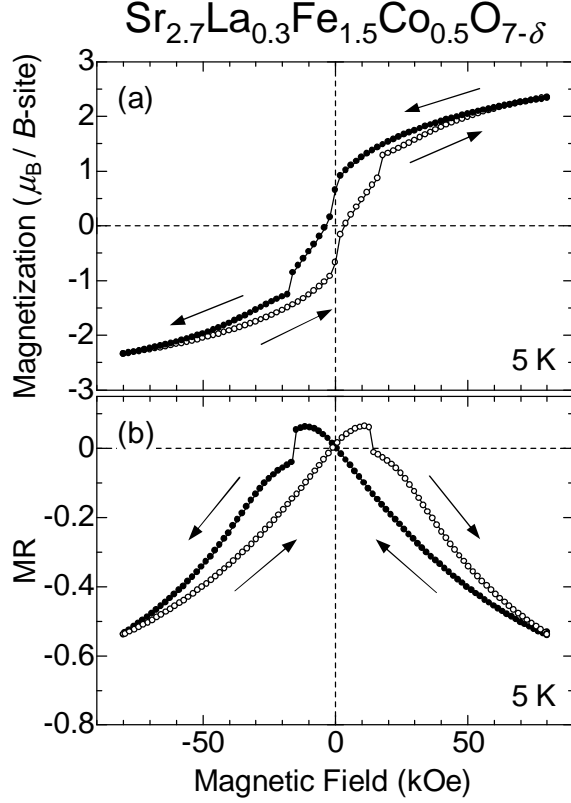


Figure 2. Magnetic field dependence of (a) magnetization and (b) magnetoresistance (MR) of $\text{Sr}_{2.7}\text{La}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ at 5 K. The arrows mean the scan directions.

Figures 1 (c) and (d) show the temperature dependence of the resistivity and MR of $\text{Sr}_{2.7}\text{Ln}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$. Here the MR value is defined as $\text{MR} = (\rho(80 \text{ kOe}) - \rho(0 \text{ kOe})) / \rho(0 \text{ kOe})$. The resistivity of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ is semiconducting, and the negative MR is observed below the onset temperature of ferromagnetism. The absolute value of MR, $|\text{MR}|$, increases gradually up to 50 % at 5 K with decreasing temperature. La^{3+} -substitution makes this system insulating, while the MR of $\text{Ln} = \text{La}$ is slightly enhanced compared with that of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ at low temperatures. With decreasing the ionic radius of Ln^{3+} , the resistivity is increasing and the $|\text{MR}|$ is further enhanced from 47 % (nondoped) to 68 % ($\text{Ln} = \text{Gd}$).

Figures 2 (a) and (b) show the M - H curve and isothermal MR of $\text{Sr}_{2.7}\text{La}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ at 5 K. A significant difference between La^{3+} -doped and nondoped samples is that a metamagnetic transition is found in the La^{3+} -doped sample around 16 kOe. The metamagnetic transition accompanies an abrupt decrease in the resistivity and is reversibly observed by applying magnetic fields. Similar metamagnetic behavior is observed in all the Ln^{3+} -substituted samples, but not in the nondoped sample.

We discuss the origin of the enhancement of the MR of $\text{Sr}_{2.7}\text{Ln}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$. We confirmed that the δ of the Ln^{3+} -substituted sample almost coincides with that of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ by iodometric titration. In other words, Ln^{3+} -substitution merely decreases the average valence of the B -site cation. An oxygen-vacancy ordered structure (or oxygen stoichiometry) might exist in the vicinity of $\delta = 0.20$. Such a decrease in the average valence of the B -site cation probably creates antiferromagnetic (AFM) (or non-FM) clusters around Ln^{3+} . It is therefore reasonable to conclude that the suppression of ferromagnetism by Ln^{3+} -substitution is due to the creation of these AFM (or non-FM) clusters. The volume reduction of the FM clusters and randomness due to Ln^{3+} -substitution cause the resistivity to be insulating. The FM clusters are aligned parallel to applied magnetic fields. As a result, the large negative

MR is observed. In addition, metamagnetism accompanying a reduction in the resistivity also contributes to the enhancement of the MR at low temperatures.

4. Summary

We have investigated a quasi two-dimensional ferromagnet $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ partially substituted by Ln^{3+} . This substitution of Ln^{3+} suppresses ferromagnetism and causes the system to be more insulating, which are attributed to an increase in AFM clusters created around Ln^{3+} . In $\text{Sr}_{2.7}\text{Gd}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$, the MR value is enhanced by about 20 % compared with that of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$. Competition between FM and AFM (or non-FM) clusters is essential for the enhancement of the MR. One of the plausible explanations for the origin of this enhanced MR is as follows. When applying magnetic fields to $\text{Sr}_{2.7}\text{Gd}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$, the FM clusters are aligned in the same direction, resulting in a reduction in resistivity. In addition, in the Ln^{3+} -doped samples, a metamagnetic transition accompanying an abrupt decrease in the resistivity occurs at low temperatures, which also contributes to the enhancement of the MR of $\text{Sr}_{2.7}\text{Ln}_{0.3}\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$.

Acknowledgments

This work was partly supported by the Asahi Glass Foundation, and Grant-in-Aid for scientific research (C) from the Japan Society for Promotion of Science.

References

- [1] Ghosh S and Adler P 2000 *Solid State Commun.* **116** 585
- [2] Breard Y, Michel C, Maignan A, and Raveau B 2001 *Solid State Commun.* **118** 517
- [3] Kuzushita K, Morimoto S, Nasu S, and Nakamura S 2000 *J. Phys. Soc. Jpn.* **69** 2767
- [4] Ghosh S and Adler P 2002 *J. Mater. Chem.* **12** 511